

Kinetics of vanadium reduction from slags by solid carbon

A V Klimov

Institute of New Materials and Technologies, Ural Federal University named after the First President of Russia B N Yeltsin, 19, Mira str., Yekaterinburg, 620000, Russia

E-mail: a.v.klimov@urfu.ru

Abstract. The laboratory investigation results of the vanadium reduction are presented. Experiments were performed with $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-V}_2\text{O}_3$ slags in an air atmosphere. The solid carbon was used as a reducing agent. The reduction kinetics was studied by sampling. It has been shown that reduction proceeds to VC carbide. The process rate is inversely proportional to the slag viscosity. The formation of a carbide film on the carbon surface leads to a sudden, by an order of magnitude, reduction in the rate. The process of vanadium reduction from oxide melts by solid carbon is electrochemical in nature and is limited by the stage of carbon anodic oxidation. The influence of slag viscosity on the process kinetics is explained by the fact that it is controlled by the growth rate and removal of gas bubbles. The appearance of the carbide film, apparently, transfers the reduction process into the intra diffusion mode, when the transfer of carbon and vanadium through the carbide film is limiting.

1. Introduction

To predict the progress of technological processes for the vanadium reduction it is necessary to have a physicochemical model of ones. From the physicochemical point of view, the question of the vanadium reduction kinetics from liquid slags by solid carbon-containing materials is practically studied insufficiently. So, the reduction of V_2O_5 and V_2O_3 from liquid slags with solid carbon was investigated by the gravimetric method [1, 2]. The experiments were carried out on slag (wt.%) 35CaO, 30SiO₂, 10Al₂O₃, 10MgO, 15CaF₂. Within 15–20 minutes after the experiment started, the process slowed down significantly. A change in the V_2O_3 slag content affected the rate much more strongly than a change in the V_2O_5 content. The first order of reaction for V_2O_5 was found, which was confirmed in [3]. Although the authors themselves [1, 2] expressed the opinion that the reduction process is limited by the stage of carbon anodic oxidation, and therefore the concentration of vanadium is not included in the kinetic equation. Reduction of vanadium oxide by carbon in stainless steel slags with Fe and Cr oxides was investigated by the authors [4]. In general, the vanadium reduction process by solid carbon continues to remain insufficiently studied, in particular, the influence of the slag composition on the reduction rate has not been disclosed. Although an attempt was made to evaluate the effect of temperature and slag composition on the process rate [5]. Our investigations have revealed a number of evidences that make it possible to reason the mechanism of vanadium reduction from slag by solid carbon and to describe the rate of the process depending on the oxide melt viscosity.



2. Experimental procedure and materials

The initial compositions of the investigated slags are presented in Table 1. A certain amount of V_2O_3 (slags 1–4) or V_2O_5 (slags 5–8) was added to them. The experiments were carried out in graphite crucibles. A thoroughly mixed mixture of a given composition oxides a particle size of less than 0.1 mm was placed in the crucible. Part of the crucible was isolated from the slag by an inserted corundum tube, which ensured the constancy of the working surface during foaming of the slag. The furnace was heated at about 100° above the temperature set for the experiment. The temperature was controlled by the tungsten-rhenium thermocouple. The crucible with the mixture was heated in the upper part of the furnace and lowered into the working zone. In this case, it took two minutes to melt the slag and establish the required temperature. After that, sampling was started by freezing on a tungsten rod. Quenching of the sample was carried out under water.

Table 1. The initial compositions of the investigated slags (wt.%).

No.	CaO	SiO ₂	Al ₂ O ₃	MgO	t, °C
1	45	35	20	–	1550
2	50	30	20	–	1550
3	55	25	20	–	1550
4	35	45	20	–	1550
5	41	23	28	8	1500
6	44	24	24	8	1550
7	32.5	18	43.5	6	1600
8	43	–	51	6	1530

3. Results and discussion

Figure 1 shows that the V_2O_3 concentration changed linearly with time. In this case, two main parts are distinguished on the curve: in the initial period of the experiment, there is a strong decrease in the V_2O_3 slag concentration, and then the process sharply slows down so that a bend appears on the $(\%V_2O_3)$ vs τ line. This type of dependence is possible if the reducing agent surface is blocked by the reaction products. Indeed, at the slag – crucible interface, a vanadium carbide film was formed, mainly consisting, as shown by X-ray diffraction studies, of VC carbide. As can be seen from the Table 2 the appearance of a carbide film significantly reduces the vanadium reduction rate. The presence of one linear part for slag 8 is explained by a low reduction rate. The amount of vanadium which was reduced during the experiment to carbide was insufficient to completely close the crucible reaction surface.

A comparison of the process rates in experiments 1–4 with ones in experiments 5–8 shows that they are practically independent of the added vanadium form and the initial vanadium concentration in the slag. Apparently, under conditions of experience at high temperatures, the transition of vanadium to the lower valence states was in time. Another reason for this fact may be that the limiting stage of the process is not related to the discharge of vanadium ions.

To identify the rate dependence on the slag composition, according to reference data [6, 7], the viscosity of the slag used in the experiments was estimated. The influence of V_2O_3 and V_2O_5 additives on slag viscosity was neglected. Figure 2 shows the dependence of the vanadium rate in both sections on viscosity in the coordinates v_v , $1/\mu$. It turned out that the reduction rate in the first linear part is inversely proportional to viscosity, and in the second linear part after the bend, it is independent of viscosity. The absence of a connection between the reduction rate and the dynamic slag characteristics indicates that in the latter case the process is limited by reasons not related to slag, in particular, probably, with the diffusion of carbon and vanadium through carbide phase.

The dependence of the reduction rates on the slag viscosity in the initial sections is related to the anodic oxidation of carbon as a limiting stage. As was shown by us in [8], the rate of anodic oxidation of solid carbon in viscous slag can be determined by the rate of growth and removal of gas bubbles, which is inversely proportional to the melt viscosity.

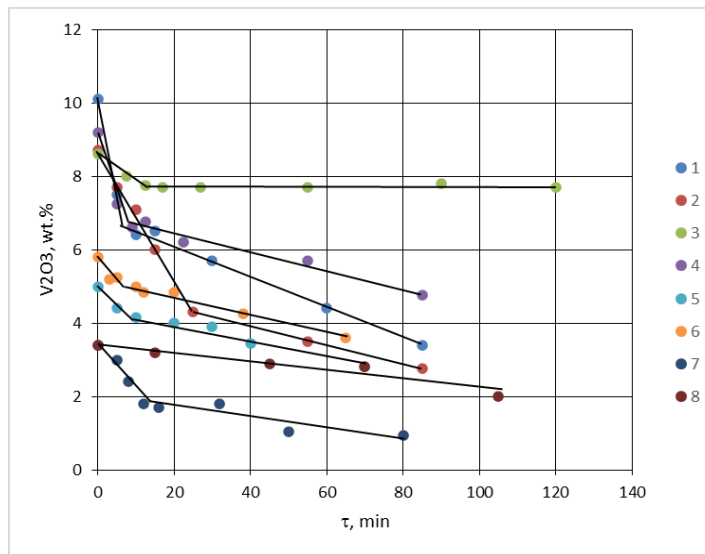


Figure 1. V_2O_3 concentration change over time during reduction by crucible carbon (line numbers correspond to the numbers of slags).

Table 2. Vanadium reduction rates, $\text{mol}/(\text{cm}^2 \cdot \text{s})$.

No.	$v \cdot 10^8$ for the first part	$v \cdot 10^8$ for the second part
1	37.3	1.38
2	14.7	7.45
3	87.2	0
4	58.5	6.94
5	82.2	7.79
6	57.0	8.65
7	56.5	5.92
8	1.14	—

The presented results differ significantly from the case when vanadium is reduced simultaneously by an iron-carbon melt and crucible carbon. As shown in Figure 3, in this case, a line bend associated with carbide formation is not observed up to a deep (90–95%) reduction of vanadium. Concentration curves quietly reach equilibrium. These facts can be explained if we assume that the reduction of vanadium from slag by solid carbon is limited by the anode half reaction



In the metal melt presence in the system, this reaction goes at the metal-slag interface, or carbon oxidation goes at the metal-graphite interface, so blocking of the crucible surface by carbides does not affect the process rate.

The initial reduction rate of vanadium by a saturated iron-carbon melt in terms of a mole of vanadium is approximately twice as high as that of solid carbon.

When expressing the viscosity μ in $\text{Pa} \cdot \text{s}$, the equation of the rate, expressed in $\text{mol}/(\text{cm}^2 \cdot \text{s})$, has the form

$$v = \left(\frac{28,879}{\mu} - 27,572 \right) 10^{-8} \quad (2)$$

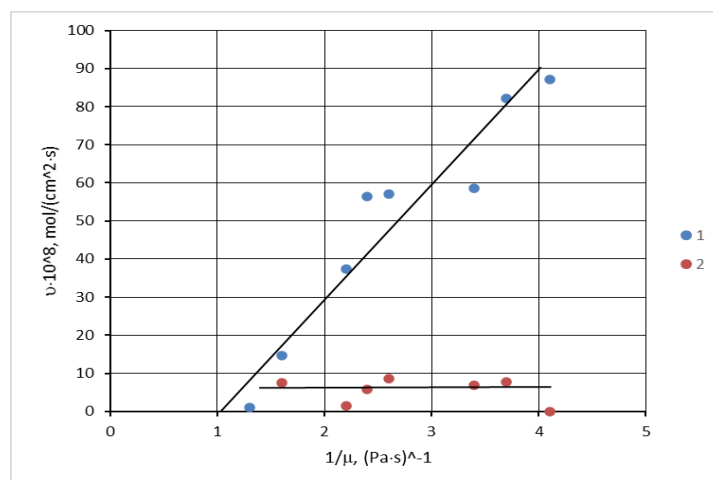


Figure 2. Dependence of the vanadium reduction rate on slag viscosity.

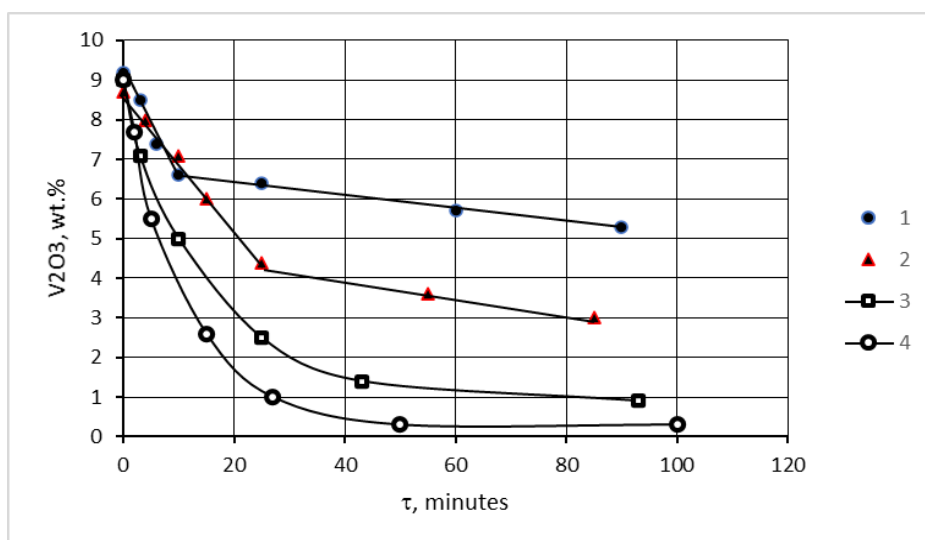


Figure 3. Change in V_2O_3 concentration with time in slags (wt.%) 35 CaO, 45 SiO_2 , 20 Al_2O_3 (1,3) and 50 CaO, 30 SiO_2 , 20 Al_2O_3 (2,4) with the V_2O_3 addition in graphite crucibles without (1, 2) and in the presence of metal (3, 4).

4. Conclusions

Thus, the presented results make it possible to discuss in more detail the mechanism of vanadium reduction from liquid slags by solid carbon, and also indicate the decisive role of slag viscosity in the process kinetics. The latter is explained by the fact that the process is controlled by the growth and removal rate of gas bubbles during anodic oxidation of carbon.

References

- [1] Lyamkin S A 1973 *Kinetics of joint metals reduction from slag by solid carbon* Ph.D dissertation [in Russian] Ural Polytechnic Institute, Yekaterinburg.
- [2] Boronenkov V N 1974 *Kinetics of metal reduction from oxide melts*, Ph.D dissertation [in Russian] Ural Polytechnic Institute, Yekaterinburg.
- [3] Vostryakov A A, Lepinskykh B M and Neuymin A D 1971 *Transactions of IMET UFAN USSR* [in Russian] (Sverdlovsk: UFAN RAN) **25** p 134
- [4] Mantha Divakar, Marten Görnerup and Ashok Kumar Lahir 2001 *Steel Research* **72** 2 pp 40–3

- [5] Cai B, Hu B, Zhao H, Guo H and Liu J 2012 *CNKI Journal Hebei Metallurgy*
- [6] Voskoboinikov V G, Dunaev N E et al. 1975 *Properties of liquid blast furnace slags: reference book* [in Russian] (Moscow: Metallurgy)
- [7] Mazurin O V, Streletsina M V and Shvaiko-Shvaikovskaya T P 1977 *Properties of glasses and glass-forming melts: Reference book* [in Russian] (Leningrad: Nauka).
- [8] Klimov A V 2011 *Transactions of XIII Russian Conference 'Structure and Properties of Metallic and Slag Melts. Vol. 3'* (Ekaterinburg: Ural Branch of the Russian Academy of Sciences) p 44